

RESERV

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Interesterification of Fatty Acid Esters

We, EASTMAN KODAK COMPANY, a company organized under the laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, (Assignee of GEORGE YOUNG BROKAW), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the interesterification of mixtures of substantially fully esterified fatty acid esters of monohydric or polyhydric alcohols to rearrange the fatty acid radicals in such fatty acid esters.

For many years, partial esters of polyhydric alcohols have been readily prepared by alcoholysis of a fatty acid ester of a polyhydric alcohol with either a monohydric or a polyhydric alcohol in the presence of an acidic or a basic catalyst. The preparation of substantially completely esterified fatty acid esters of suitably modified characteristics by the rearrangement of fatty acid radicals between full esters has been more difficult, however, because of the lack of suitable methods for effecting the reaction easily and in high yield. As a consequence, it has been necessary to resort to indirect methods rather than effecting direct cross-esterification between substantially completely esterified fatty acid esters. For example, the preparation of mixed esters such as the triglycerides containing both lower and higher fatty acid radicals has been accomplished by first making glyceryl partial esters of the higher fatty acids and then acetyating these partial esters either by an alcoholysis reaction or by reacting the partial ester with an anhydride such as acetic anhydride.

Another method which has been employed involves adding a minor amount of a polyhydric alcohol to a mixture of substantially fully esterified fatty acid esters whereby the rearrangement of the fatty acid radicals results

from a succession of incremental alcoholysis reactions. It is desirable, however, to provide an interesterification process which proceeds directly between substantially fully esterified fatty acid esters with the same ease and facility as is the case in alcoholysis reactions. For this, the conventional alcoholysis catalysts have proved largely ineffective.

The cross-esterification of substantially completely esterified fatty acid esters is highly desirable in many cases. It is very useful in modifying the physical and chemical characteristics of the triglyceride fats, which include both solid fats and fatty oils. Thus, for example, the animal fats such as lard and the vegetable oils such as soybean oil, cottonseed oil, coconut oil, whether unhydrogenated or partially or fully hydrogenated, consist largely of mixtures of triglycerides, and their properties can be modified to make them more suitable for particular applications by rearranging the fatty acid radicals in the mixture. Similarly, full esters of certain predetermined characteristics can be prepared by effecting ester interchange between a substantially completely esterified fatty acid ester of a polyhydric alcohol and a different fatty acid ester of the same or different polyhydric alcohol or of a monohydric alcohol. Also mixed esters of polyhydric alcohols with higher and lower fatty acids have properties quite dissimilar to those of the esters of a polyhydric alcohol with all higher fatty acids.

It is accordingly an object of this invention to provide a new method of effecting direct ester-interchange in mixtures of substantially completely esterified fatty acid esters.

According to the present invention, a method of effecting interesterification comprises heating a mixture of substantially completely esterified fatty acid esters at a temperature of at least 180° C. in the presence of a plural metal soap catalyst comprising a soap or soaps of at least two metals wherein one

of the metals is an alkali or an alkaline earth metal and the other metal is an amphoteric metal, and thereby rearranging the fatty acid radicals in the mixture, said soap or soaps being derived from one or more fatty acids having at least 5 carbon atoms per molecule.

The fatty acid esters may be esters of either polyhydric alcohols such as glycerol, glycols such as ethylene glycol, propylene glycol and 10 polyalkylene glycols, cellulose, sorbitol, mannitol, pentaerythritol, or polyvinyl alcohol or of monohydric alcohols such as methanol, ethanol, propanol, or butanol. The fatty acid radicals in such fully esterified esters can be saturated 15 or unsaturated fatty acid radicals, and are typified by acetates, propionates, butyrates, valerates, caproates, caprylates, caprates, laurates, myristates, palmitates, stearates, arachidates, behenates, carnaubates, cerotates, 20 montanates, oleates, sorbates, linoleates, lininates, and elaidates. In the case of the fully esterified fatty acid esters of polyhydric alcohols, the alcohol can be esterified with the same or different fatty acids. The fatty acid 25 radicals can be of either higher or lower fatty acids ranging from two carbon atom fatty acids to  $C_{22}$  or  $C_{24}$  fatty acids, or even  $C_{50}$  acids or higher.

In practicing the invention, the processes 30 embodying the invention can be utilized for treating mixtures of substantially fully esterified esters of two different polyhydric alcohols having dissimilar fatty acid radicals, or of the same polyhydric alcohols containing different 35 fatty acid radicals, to form mixed esters. Similarly one of the fatty acid esters can be a fully esterified polyhydric alcohol e.g. a fatty acid triglyceride and the other fatty acid ester can be the ester of a monohydric alcohol. In 40 like manner mixtures of fatty acid esters of monohydric alcohols can be processed in accordance with the invention.

The plural metal soap catalysts can be added 45 to the mixture of fatty acid esters in the form of a double metal soap, that is, as a double metal salt of a higher fatty acid, i.e. a salt of a fatty acid having at least five carbon atoms and more desirably at least eight carbon atoms, or in the form of soaps of the individual metals, 50 or in the form of separate alkali or alkaline earth metal compounds and amphoteric metal compounds capable of reacting in the reaction mixture to form the requisite soaps of the two metals and the term "plural metal soap catalyst" is intended to cover those formed *in situ* 55 as well as those added in the soap form, and those present as mixtures of individual metal soaps as well as a double metal soap. When the catalyst is formed *in situ*, at least one of the metal compounds and desirably both of the metal compounds employed should be at 60 least partially soluble in the mixture of fatty acid esters under the reaction conditions to facilitate formation of the soap catalyst. Alternatively, one of the metal compounds can be in

the form of a metal soap and the other metal compound in a form capable of supplying the metal ions necessary for formation of the plural metal soap catalyst of the invention.

One of the metals in the plural metal soap catalyst must be either an alkali metal or an alkaline earth metal, such as sodium, potassium, lithium, caesium, calcium, strontium or barium. The other of such metals is an amphoteric metal and suitable amphoteric metals include aluminium, titanium, zirconium, cerium, tin, lead, cobalt, molybdenum, manganese, cadmium, iron, copper, chromium, vanadium, thallium, nickel, platinum, palladium and zinc although any of the amphoteric metals characterised by the ability to act as cations or to form a metal-bearing anion can be used.

While any of the plural metal soap catalysts defined hereinabove can be employed, those catalysts having aluminium as the amphoteric metal component are preferred and the alkali metal-aluminium soaps are most desirable. The aluminium containing soaps can be used in smaller amounts than the other catalysts since they exhibit the highest degree of catalytic activity in the interesterification reactions embodying the invention.

Another preferred class of catalysts embodying the invention is that in which the amphoteric metal is titanium. In the case of titanium soaps, however, larger amounts are ordinarily employed than in the case of the aluminium soaps. The remaining plural metal soap catalysts are entirely suitable and give excellent results when used in amounts of four times or as much as eight times the amount of the aluminium-containing plural metal soaps. The plural metal soap catalysts wherein aluminium is the amphoteric metal are desirably employed in amounts of about 0.01 moles of catalyst per kilogram of reaction mixture although amounts as low as 0.001 moles per kilogram or lower can be used and higher amounts are not objectionable but usually are not necessary.

Typical examples of suitable double metal soaps wherein both metals are included in a single soap which can be either formed *in situ* by the inclusion of separate metal compounds or added as a pre-formed double metal soap include lithium aluminium stearate, lithium aluminium palmitate, sodium aluminium oleate, sodium titanium stearate, lithium titanium palmitate, potassium aluminium myristate, lithium zirconium linoleate, calcium aluminium stearate, strontium titanium palmitate, sodium zirconium stearate, lithium cerium oleate, sodium cobalt stearate, calcium titanium palmitate, barium aluminium stearate, lithium zinc myristate, potassium titanium palmitate, sodium cadmium linoleate, lithium lead stearate, and potassium copper stearate although any of the other plural metal soaps as described hereinabove can be employed satisfactorily in accordance with the invention.

When the soap is formed *in situ*, it will, of course, be a mixture of soaps depending upon the fatty acids present in the reaction mixture.

When the metal compounds forming the catalyst are added separately and the soaps are formed in the reaction mixture, one or both of the metals can be readily added in the form of an alcoholate such as the methoxide, ethoxide or isopropoxide, or in the form of a salt of a fatty acid such as a stearate, palmitate, or oleate, or as an oxide, chloride or hydroxide of the metal, when such compounds can furnish the metal in a form available for soap formation under the reaction conditions. The nature of the metal compound added is not a factor in the process embodying the invention providing the metal compound is in a form capable of entering into the soap formation in the fatty acid ester mixture being processed in accordance with the invention. It has been found that most of the metals which act so effectively as catalyst in the combination defined herein are largely ineffective to catalyse interesterification when employed alone. The inclusion of more than one metal from the amphoteric metal group or from the alkali and alkaline earth group or both can be done if desired and is within the scope of this invention, although this is not necessary for optimum results as long as one metal from each group is present. The term "plural metal soap catalyst" thus is not intended to limit the invention to the inclusion of only two metals in the reaction mixture but refers instead to the two classes of metals which must be present.

When the catalyst is formed in the reaction mixture, it is desirable but not necessary to add the metal-containing components in a mole for mole ratio. The amount of catalyst employed can be varied widely and amounts as low as 0.05% or lower based on the weight of fatty acid esters being treated can be used. For commercial operations, concentrations of catalyst of the order of 0.1 to 0.5% have been found to be highly effective, although amounts as high as 1% or even 5% can be used but are usually not necessary. On a molar basis, catalyst concentrations of about 0.01 moles per kilogram of charge are preferred. The interesterification embodying the invention is effected at a temperature of at least 180° C. and desirably at a temperature of at least 200° C. Optimum results are obtained in the range of about 230° C. to 260° C. in most cases, although temperatures as high as 300° C. or higher have been used and may be desirable in some cases. The catalyst in some cases may be in the form of a mixture of a double metal soap formed *in situ* together with two individual metal soaps added to the reaction mixture, the exact nature of the soap catalyst and whether it is a mixture of soaps or a single double metal soap is not critical providing at least one member of each group of metals as defined is present in soap form.

A particular advantage of the catalysts employed in practicing this invention is their high catalytic activity under reaction conditions and their inactivity at temperatures below 180° C. and usually below 200° C. This makes it possible to effect cross-esterification in a mixture of fully esterified fatty acid esters at a temperature at or above 180° C., usually above 200° C., until the desired rearrangement of fatty acid radicals has been effected and then cool the reaction mixture down to a temperature below 180° C. usually 200° C. at which the catalyst is inactive and separate out the desired product or products without causing further rearrangement as the equilibrium becomes unbalanced by withdrawal of product. When a particular product is being separated out, the depleted mixture can then be replenished with additional ester and again heated to reaction temperature whereupon the catalyst again becomes active. This also makes it possible to effect any desired degree of rearrangement in the reaction mixture by control of the temperature and the time of heating, and the reaction can be stopped at a predetermined stage by simply cooling the reaction mixture. Thus, for example, the properties of a triglyceride fat, including both the animal fats and the vegetable oils, can be altered to any desired degree and the product then recovered without further change by means such as vacuum distillation, solvent extraction, or fractional crystallization at temperatures below the temperature at which the catalyst is active.

The invention is particularly useful for modifying the characteristics such as melting point, freezing point or crystallization characteristics of triglyceride fats and fatty oils such as lard, butter, butter oil, tallow, and cocoa butter, unhydrogenated or partially or fully hydrogenated vegetable oils such as soybean oil, peanut oil, coconut oil, cottonseed oil, and corn oil or of mixtures of these or other fats and fatty oils consisting predominantly of fatty acid triglycerides.

Another particularly suitable use for the invention is in preparing fatty acid full esters of polyhydric alcohols wherein the alcohol e.g. glycerine is esterified with both higher and lower fatty acids. Thus, for example, triacetin or tributyrin or a similar ester of a lower fatty acid having less than 5 carbon atoms per molecule can be reacted with a higher fatty acid ester in which the fatty acid contains more than 5 carbon atoms per molecule, i.e. 6 to 24 or more carbon atoms per molecule, such as tripalmitin, triolein, tristearin, oleodipalmitin, stearodilaurin, or palmitodistearin, to give products containing one or more lower fatty acid radicals and one or more higher fatty acid radicals. Typical of such products are monoacetodistearin, diacetomonostearin, monobutyrodipalmitin, monobutyrodistearin, diacetomonopalmitin, monoacetodiolein, monobutyro-

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diolein, diacetomono-olein or mixtures of these compounds.

Similarly, a triglyceride fat, such as an animal fat or a vegetable oil, whether unhydrogenated or partially or fully hydrogenated and consisting of a mixture of fatty triglycerides can be cross-esterified with triacetin or tributyrin to give greatly modified materials. Likewise, the triglycerides can be cross-esterified with fully esterified glycols or with fatty acid full esters of other polyhydric alcohols. Lard and hydrogenated lard can be cross-esterified to give a product having properties differing from both reactants. Low melting or liquid fats can be inter-esterified with a pure triglyceride like tristearin to give products intermediate between the fat and the tristearin. It is thus evident that any combination of fully esterified fatty acid esters can be used, and that the interesterification is useful for a vast number of applications in the ester field.

In practicing the invention, the mixtures being treated need not be anhydrous or acid-free. When the catalyst is formed *in situ*, the presence of free fatty acid in the mixture is actually desirable in order that the catalyst soap can be more quickly formed although an initial free fatty acid content is not necessary since the required amount of fatty acid becomes available under the reaction conditions. The reaction mixture obtained by means of this invention can be readily distilled since the double metal soap catalysts do not cause gelling during the distillation. The products obtained are readily recovered by vacuum distillation at temperatures below about 200° C. and pressures of 1-100 microns of mercury in accordance with usual distillation practice, although higher temperatures can be used without substantial reversion in the case of this film vacuum distillation even though the catalyst is active under these conditions. Thus temperatures as high as 250° C. or 260° C. or higher have been successfully employed. The catalyst need not be chemically inactivated and hence can be used repeatedly which makes large scale cyclic operations possible.

The invention is illustrated by the following examples of preferred embodiments thereof, it being understood that the examples are illustrative only and not intended to limit the scope of the invention:—

#### EXAMPLE 1.

Lithium aluminium ethylate was prepared by dissolving 5 g. of lithium aluminium hydride in 100 ml. of ether and adding the resulting solution to 100 ml. of ethanol. The resulting product was then diluted with an additional 100 ml. of ether, and 80 ml. of this solution was then added to a mixture of 200 g. of triacetin and 200 g. of hydrogenated lard. The resulting reaction mixture, after removal of the catalyst solvent, was heated for 1 hour at 250° C. (during which time a double soap

of lithium and aluminium was formed) and then cooled below 150° C. The cooled reaction mixture was vacuum distilled at a pressure below about 10 microns Hg. and the unreacted triacetin collected up to a temperature of 135° C. The fraction distilling in the range of 140-185° C. was collected and consisted predominantly of diacetomonostearin and diacetomonopalmitin together with a minor amount of the corresponding monoaceto derivatives and a small amount of acetomyristates and acetoarachidates. This product amounted to a yield of 38% as compared to a yield of but 9.5% using aluminium isopropoxide alone as catalyst.

#### EXAMPLE 2.

A recycle of the combined residue and triacetin fractions as obtained in the preceding example was run by mixing together 93 g. of the recovered triacetin fraction, 107 g. of fresh triacetin, 115 g. of the residue containing the lithium aluminium soap catalyst, unreacted hydrogenated lard, monoacetodistearin and monoacetodipalmitin, and 85 g. of fresh hydrogenated lard. This mixture was heated for 1 hour at 250° C. and then cooled below 150° C. No additional catalyst was added for the recycle operation. The resulting product was then vacuum distilled as before and a 45.6% yield of purified product was obtained consisting predominantly of diacetomonostearin and diacetomonopalmitin.

#### EXAMPLE 3.

To a mixture consisting of 200 g. of hydrogenated lard and 200 g. of triacetin was added 1.57 g. of aluminium isopropoxide and 0.25 g. of lithium isopropoxide. The resulting mixture was heated at 250° C. for 1 hour, cooled and vacuum distilled. The diacetomonostearin-diacetomonopalmitin fraction distilling at 140-185° C. was collected in a yield of 40.3%. It is thus apparent that the metals which form the catalyst can be added separately and the soap or soaps constituting the plural metal catalyst formed *in situ*.

#### EXAMPLE 4.

The plural metal catalyst was furnished by adding 1.09 g. of lithium stearate and 6.93 g. of aluminium stearate to a mixture of 200 g. of hydrogenated lard and 200 g. of triacetin. After heating for 1 hour at 250° C., the product was cooled and vacuum distilled as described hereinabove to give a 45.3% yield of the mixed diaceto ester. The residue was replenished and recycled five times without the addition of fresh catalyst and a 40% yield obtained on the fifth recycle. The catalyst thus remains in the residue with undiminished catalytic activity throughout repeated reactions.

#### EXAMPLE 5.

An unsuccessful attempt at interesterifica-

tion was made by heating a mixture of 200 g. of hydrogenated lard, 200 g. of triacetin and 1.09 g. of lithium stearate alone as catalyst. A similar unsuccessful run was made with 6.93 g. of aluminium stearate as sole catalyst. The residue and distillate fractions from these two unsuccessful reactions were then combined and heated at 250° C. for one hour. A 39.2% yield of interesterified product was obtained by vacuum distillation.

**EXAMPLE 6.**  
A sodium aluminium soap catalysis was effected by mixing together 200 g. of hydrogenated lard, 200 g. of triacetin, 0.009 g. of sodium methoxide and 1.65 g. of aluminium stearate and heating the resulting mixture for 1 hour at 250° C. Distillation gave 173 g. of interesterified product distilling in the range of 135° to 185° C. under the distillation conditions.

**EXAMPLE 7.**  
A batch of 200 g. of lard, 200 g. of triacetin, 0.0068 g. of sodium hydroxide and 0.382 g. of aluminium isopropoxide was heated for 1 hour at 250° C. during which time a double soap of sodium and aluminium was formed. Vacuum distillation gave a 37.6% yield of interesterified aceto-olein product. The residue was replenished with additional lard and triacetin but no additional catalyst. After heating and distilling as before, a 41.7% yield of mixed ester was obtained.

**EXAMPLE 8.**  
A 200 g. batch of unbleached lard which was partly liquid at 25° C. was charged into a pot still and 0.54 g. of lithium stearate and 1.65 g. of aluminium stearate were added. The resulting mixture was then heated at 250° C. and a pressure of 3 microns for 1 hour. The interesterified reaction product was solid at 25° C. and had a melting point of 27°-39° C. This product was then filtered at 26.5° C. and gave 31.1% of solid fat having a melting point of 41°-47° C. and 66.7% of liquid fat having a cloud point of 10° C.

**EXAMPLE 9.**  
Cottonseed oil having a cloud point of 11° C. was interesterified by heating 578 g. of the oil with 0.78 g. of lithium stearate and 2.39 g. of aluminium stearate at 250° C. The product was filtered and bleached to give an interesterified oil having a cloud point of 19° C.

**EXAMPLE 10.**  
A 400 g. batch of soybean oil having a cloud point of -6° C. was heated at 250° C. with 0.54 g. of lithium stearate and 1.65 g. of aluminium stearate. The reaction product after filtering and bleaching was a clear yellow oil having a cloud point of 3° C.

**EXAMPLE 11.**  
A 400 g. batch of menhaden oil, from a lot which gave a 49.2% distillate (iodine value

140.7) at 278-289° C. and 10 microns pressure, was heated at 250° C. with 0.54 g. of lithium stearate and 1.65 g. of aluminium stearate. The resulting interesterified oil had a 50.5% distillate fraction distilling over a range from 220-290° C. and having an iodine value of 122.

**EXAMPLE 12.**

Hydrogenated lard and triacetin in equal proportions by weight were interesterified with 0.00935 moles per kilogram of charge of a strontium aluminium soap catalyst formed *in situ* by the addition of strontium hydroxide and aluminium stearate at 250° C. The product was distilled and the resulting diacetomonostearin-diacetomonopalmitin mixed esters recovered.

**EXAMPLE 13.**

Diacetylated esters of hydrogenated lard were prepared as in the preceding example using 0.138 g. of calcium hydroxide and 1.65 g. of aluminium stearate to provide a calcium aluminium soap catalyst.

**EXAMPLE 14.**

Mixed butyrostearins were prepared by heating a mixture of 275 g. of tributyrin, 550 g. of hydrogenated lard, 1.12 g. of lithium stearate, and 3.36 g. of aluminium stearate at 255° C. for 1 hour. The resulting reaction mixture was then vacuum distilled at about 10 microns pressure. A 317 g. fraction consisting predominantly of dibutyromonostearin and having a saponification value of 331 was recovered in the temperature range of 135-210° C. a 200 g. fraction consisting predominantly of monobutyrotriglycerides having a saponification value of 251 was distilled over in the range of 210-240° C. The melting point of the dibutyromonostearin was 7-16° C., and the melting point of the "monobutyrodistearin" was 31.5-32.5° C.

**EXAMPLE 15.**

Interestesterification between hydrogenated coconut oil and triacetin was effected by heating a mixture of 1006 g. of hydrogenated coconut oil, 994 g. of triacetin, 2.72 g. of lithium stearate and 8.16 g. of aluminium stearate at 250° C. for 1 hour. The product was distilled to give 237 g. of diacetylated coconut oil esters consisting predominantly of diacetomonolaurin and diacetomonomyristin and 216 g. of monoacetylated esters consisting predominantly of monoacetodilaurin, monoaceto-dimyristin, and acetolauromyristin.

**EXAMPLE 16.**

Compositions containing large amounts of dibutyromono-olein and of monobutyrodiolein together with smaller amounts of the butyrostearins and butyropalmitins were prepared by interesterifying 666 g. of unhydrogenated lard with 334 g. of tributyrin in the presence of 1.36 g. of lithium stearate and 4.08 g. of aluminium stearate at 250° C. The reaction product was distilled at 10 microns pressure and the unreacted tri-butyryl removed at tempera-

tures up to 135° C., 359 g. of a composition consisting predominantly of dibutyrotriglycerides were recovered in the range of 135—200° C. and 301 g. of a composition consisting predominantly of monobutytritriglycerides were distilled over in the range of 200—240° C. The dibutyrotriglycerides composition had a saponification value of 332, a cloud point of —0.8° C. and a freezing point of —20° C.

10 The monobutyrotriglycerides composition has a saponification value of 247, a cloud point of 9.5° C. and a freezing point of 4—5° C. The "butyro-oleins" and "aceto-oleins" which are liquid at room temperature find excellent utility as plasticizers and as diluents for hard fats to increase their plasticity range.

EXAMPLE 17.

20 Hydrogenated lard and triacetin in equal proportions by weight were interesterified at 250° C. by means of 0.055 moles per kilogram of reaction mixture of a sodium zinc soap catalyst resulting in the reaction mixture from the addition of sodium hydroxide and zinc palmitate, and the resulting mixed esters were recovered by distillation as described in preceding examples.

EXAMPLE 18.

30 Hydrogenated lard and triacetin in equal proportions by weight were interesterified as described in Example 17 by means of 0.073 moles per kilogram of reaction mixture of a lithium cobalt soap catalyst resulting from addition of lithium stearate and cobalt stearate to the reaction mixture.

EXAMPLE 19.

35 Hydrogenated lard and triacetin in equal proportions by weight were interesterified as described in Example 17 using 0.00935 moles of a strontium aluminium soap catalyst per kilogram of reaction mixture resulting from addition of strontium hydroxide and aluminium stearate to the reaction mixture.

EXAMPLE 20.

40 The interesterification of hydrogenated lard and triacetin in equal proportions by weight in accordance with the procedure detailed hereinabove (Example 17) was effected with 0.0374 moles per kilogram of reaction mixture of a sodium titanium soap catalyst added in the form of sodium hydroxide and titanium ethylate.

EXAMPLE 21.

45 The interesterification of hydrogenated lard and triacetin in equal proportions by weight was effected as in Example 17 with 0.0187 moles per kilogram of reaction mixture of a lithium titanium soap catalyst from the addition of lithium stearate and titanium ethylate to the reaction mixture.

EXAMPLE 22.

50 A lithium manganese soap catalyst formed by addition of lithium stearate and manganese stearate to the reaction mixture was used to interesterify hydrogenated lard and triacetin in equal proportions by weight using 0.00935

moles of catalyst per kilogram of reactants and following the procedure of Example 17.

EXAMPLE 23.

55 A lithium tin soap catalyst from addition of lithiumstearate and tin acetate to the reaction mixture catalyzed the interesterification of hydrogenated lard and triacetin in equal proportions by weight using 0.00935 moles of catalyst per kilogram of reactants and following the procedure of Example 17.

EXAMPLE 24.

60 A lithium vanadium soap catalyst was used to catalyze the interesterification of hydrogenated lard and triacetin at 250° C. 0.00935 moles of catalyst were used per kilogram of reactants, the latter being in equal proportions by weight.

EXAMPLE 25.

65 The interesterification at 250° C. of hydrogenated lard and triacetin in equal proportions by weight was catalyzed by 0.00935 moles per kilogram of reactants of a lithium chromium soap catalyst resulting from addition of lithium stearate and chromium stearate to the reaction mixture.

EXAMPLE 26.

70 Similar interesterification is effected with esters of monohydric alcohols. Thus 300 g. of coconut oil and 100 g. of ethyl stearate were mixed together and heated for 1 hour at 250° C. in admixture with 0.54 g. of lithium stearate and 1.65 g. of aluminium stearate. The reaction mixture was then heated at 256° C. and a pressure of 10 mm. Hg. and 46.3% of low boiling ethyl esters of fatty acids such as capric, caproic and lauric acids, having a saponification value of 251 were distilled off.

75 The residual mixture consisting largely of rearranged triglycerides was then charged to a centrifugal high vacuum still. This residue was a solid having a saponification number of 249. A liquid fraction weighing 22.0 g. was collected at a temperature of 180° C. and a pressure of 7 microns Hg.; a second liquid fraction weighing 46.4 g. was distilled out at 210° C. and a pressure of 5 microns Hg. and a third liquid fraction of 39.5 g. was distilled out at 220° C. and 5 microns Hg. pressure. At 240° C. and a pressure of 3 microns Hg., a 144.5 g. fraction of normally solid product was obtained, and a 30.5 g. fraction of solid product was obtained at 250° C. and 3 microns Hg. pressure. The residue was a solid weighing 22.0 g. Thus, the characteristics of the coconut oil were altered by the interesterification with a simple ester of a monohydric alcohol.

EXAMPLE 27.

80 Coconut oil was modified in a still different fashion by interesterifying 300 g. of coconut oil with 100 g. of methyl palmitate in the presence of 0.54 g. of lithium stearate and 1.65 g. of aluminium stearate. The reaction mixture was heated for 1 hour at 250° C., and the pressure was reduced to 10 mm. Hg. and

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the temperature raised to 265° C. whereupon a 51.6 fraction of methyl ester distillate having a saponification value of 287 was obtained. The residue had a saponification value of 248. The original coconut oil had a saponification value of 246. A 327.5 g. portion of the solid residue was then distilled on a centrifugal high vacuum still. The first fraction weighing 16.5 g. was a liquid obtained at 150° C. and 25 microns Hg. pressure. A second liquid fraction weighing 4.0 g. was obtained at 200° C. and 8 microns Hg. pressure, and a third liquid fraction of 42.8 g. was obtained at 220° C. and 7 microns Hg. pressure. The next fraction of 28.1 g. obtained at 230° C. and 5 microns Hg. was a semi-solid. The fraction obtained at 240° C. and 4 microns Hg. was a solid and weighed 90.5 g. At 250° C. and 4 microns Hg., a 71.5 g. solid fraction was obtained, and a final solid fraction weighing 40.0 g. was obtained at 260° C. and 5 microns Hg. pressure. The solid residue weighed 12.5 g. As can be seen, the reaction product obtained by interesterification of coconut oil with methyl palmitate differed significantly from that obtained by interesterification with ethyl stearate as set out in the preceding example. Thus, the properties of a triglyceride such as coconut oil can be varied as desired by varying the nature of the full ester with which it is reacted in accordance with the invention as well as by changing the relative proportions of the reactants to direct the interesterification toward a desired product as contrasted with a completely randomized mixture obtained with stoichiometric proportions.

EXAMPLE 28.

Interestesterification was effected between 300 g. of pentaerythritol tetraoleate and 100 g. of triacetin in the presence of 0.54 g. of lithium stearate and 1.65 g. of aluminium stearate at 250° C. After a 1 hour reaction period, the reaction product was vacuum distilled at a pressure of 10 microns Hg. A distillate fraction amounting to 29.8% of the total charge was obtained in the range of 135°—185° C. and an additional 5% was obtained between 185° C. and 200° C. The first fraction obtained had a cloud point of —13° C., a freezing point of —30° C. and a refractive index of 1.5445 at 25° C. The modification of the physical properties of the reactants is evident for triacetin distils completely below 135° C. at 10 microns pressure whereas pentaerythritol tetraoleate distils only above 250° C. at this pressure. By the interesterification, nearly 35% of the reaction product distilled in the range of 135°—200° C.

EXAMPLE 29.

60 A mixture was prepared of 200 g. of cotton-seed oil and 200 g. of hydrogenated lard. The mixture melted rather sharply at 56—57° C. To the mixture was added 0.54 g. of lithium stearate and 1.64 g. of aluminium stearate, and the resulting reaction mixture was heated at

250° C. for one hour. Following reaction, the product was cooled to 150° C. and vacuum distilled at a pressure below 10 microns Hg. A very small fraction weighing 12 g. or 3.1% yield distilled off at 150 to 200° C. The bulk of the product (339 g. or 87.7%) distilled in the range of 200—290° C. This product had a melting point of 48.52° C. or nearly 10° C. lower than the original mixture.

EXAMPLE 30.

70 A batch of commercial coconut oil ("Cobee 76") was distilled under vacuum and 36% of the original oil was obtained as a liquid distillate product. The distilled coconut oil (i.e. the liquid distillate product) was then rearranged in accordance with this invention using a lithium aluminium soap catalyst. The catalyst was a mixture of equal proportions of lithium stearate and aluminium stearate at a concentration of 0.00935 moles of catalyst per kilogram of coconut oil. The reaction was effected at a temperature of 250° C. for a period of 1 hour. The resulting rearranged oil gave only 23.5% of distillate as a liquid fraction. Similarly a batch of unreacted coconut oil ("Koline 76") was distilled at 200° C. and 10 microns pressure. A 12% distillate fraction was obtained. After interesterification of the distillate fraction in accordance with this invention, a similar batch gave only a 3.5% distillate fraction at 200° C.

75 90 95 100 105 110 115 120 125 130

Thus by means of this invention, the properties of substantially completely esterified fatty acid esters are modified by interesterification in mixtures of such esters. Since the natural fats, including both the solid fats and fatty oils, consist largely of mixed fully esterified triglycerides of the fatty acids having from 4 to 24 carbon atoms and usually from about 8 to 22 carbon atoms in the fatty acid chain, the properties of such fats are modified by merely heating with the plural metal soap catalysts embodying the invention to rearrange the fatty acid radicals already present. The degree of rearrangement and hence the degree of modification can be varied as desired by varying the time and temperature of reaction in accordance with usual esterification practice.

When it is desired to modify the properties still further, a wholly foreign fatty acid ester can be introduced to take part in the interesterification as for example a lower fatty acid ester of glycerine such as triacetin, or tributyrin whereby some of the higher fatty acid radicals are replaced by the lower fatty acid radicals. When stoichiometric amounts of the fatty acid esters are employed, the reaction product is a randomized complex mixture of the possible combinations of radicals on the polyhydric alcohol. By varying the proportions of the reactants and the reaction conditions, the randomization equilibrium is shifted toward a desired product. Thus, for example, in a fat consisting largely of stearic

and palmitic mixed triglycerides, an excess of triacetin will direct the equilibrium towards larger amounts of diacetomonostearin and diacetomonopalmitin and lesser amounts of monoacetodistearin, monoacetodipalmitin and monoacetopalmitostearins than with a stoichiometric reaction. 5

By use of two different polyhydric alcohol esters with different fatty acid radicals, the properties of both are modified to give a randomized mixture which likewise can be directed towards one or the other of the reactants. Thus, by reacting pentaerythritol tetraoleate with triacetin, a mixed product having intermediate properties is obtained. An excess of triacetin gives a product approaching the triacetin properties whereas an excess of the pentaerythritol ester gives a product more closely approaching this latter ester. 10

This invention thus permits the preparation of full esters having properties modified to any desired degree. The cloud point of fatty oils can be raised or the melting point can be raised, or a mixture can be prepared having a much wider range of plasticity than the original fat. By suitable interesterification and fractionation of the product by vacuum distillation or fractional crystallization, modified esters of any desired melting point can be prepared and sharp melting fats can be obtained. 20

The preparation of "tailor-made" fatty esters is thus possible for use as plasticizers, coking oils, coatings, or butter or margarine substitutes with the same ease which is normally attendant to alcoholysis reactions. 25

The process embodying the invention finds equal utility with the unsaturated and the saturated mixed esters and thus can be used for rearranging the unhydrogenated fats, including animal fats and vegetable oils as well as the partially and fully hydrogenated fats depending upon the characteristics desired for the final product. 30

Thus by means of this invention, fatty esters can be readily prepared to fulfil various desired requirements depending upon the use to which they are to be put. In this way, the commercial utilization of the fatty esters is greatly advanced and the dependence upon the original properties of the natural fats and fatty oils is obviated. 40

The catalysts employed in the invention not only exhibit unusual activity in promoting interesterification, but they find particular utility in cyclic processes because they do not interfere with distillation and retain their activity through repeated recycles. Thus, a desired rearranged fraction can be removed following reaction and the residue replenished with additional reactants and run through the process any number of times. By this means, the fatty esters charged to the process are recovered in the desired interesterified form in substantially complete yield. 50

Furthermore, the catalysts used in the invention do not have to be used under anhydrous or acid-free conditions so that the reactants need not be first subjected to a costly pre-treatment before interesterification. The reaction velocities are appreciably better than were obtainable heretofore in interesterification reactions, and side reactions are greatly minimized. 55

The rearranged fatty esters prepared in accordance with this invention are not only useful directly, as described hereinabove, but also find utility in the preparation of partial esters such as monoglycerides and diglycerides by alcoholysis to give partial ester compositions with properties different from those obtainable from unmodified fats. 60

What we claim is:—

1. A method of effecting interesterification comprising heating a mixture of substantially completely esterified fatty acid esters at a temperature of at least 180° C. in the presence of a plural metal soap catalyst comprising a soap or soaps of at least two metals, wherein one of the metals is an alkali or alkaline earth metal and the other metal is an amphoteric metal, and thereby rearranging the fatty acid radicals in the mixture, said soap or soaps being derived from one or more fatty acids having at least 5 carbon atoms per molecule. 65
2. A method as claimed in Claim 1 in which the mixture of fatty acid esters includes a fatty acid ester of a polyhydric alcohol. 70
3. A method as claimed in Claim 1 in which the mixture of fatty acid esters includes a fatty acid ester of a monohydric alcohol. 75
4. A method as claimed in Claim 1 in which the mixture of fatty acid esters is a mixture of triglycerides. 80
5. A method as claimed in Claim 1 in which the mixture of fatty acid esters is a mixture of fatty acid triglyceride and a fatty acid ester of a monohydric alcohol. 85
6. A method as claimed in Claim 1 in which the mixture of fatty acid esters is a mixture of a fatty acid triglyceride and triacetin. 90
7. A method as claimed in Claim 4 in which the mixture of triglycerides includes a triglyceride of a fatty acid containing less than 5 carbon atoms per molecule and a triglyceride of a fatty acid containing more than 5 carbon atoms per molecule. 95
8. A method as claimed in Claim 1 in which the mixture of fatty acid esters is in the form of a vegetable oil or an animal fat. 100
9. A method as claimed in any one of the preceding claims in which the plural metal catalyst is added in the form of an alkali metal or alkaline earth metal compound and an amphoteric metal compound which, during the heating, form the plural metal soap catalyst which catalyses the interesterification of the mixture of fatty acid esters. 105
10. A method as claimed in any one of the preceding claims in which the alkali metal is sodium or lithium. 110

11. A method as claimed in any one of the preceding claims in which the amphoteric metal is aluminium.

12. A method as claimed in any one of the preceding claims in which the mixture of fatty acid esters is heated in the temperature range 230° C. to 260° C.

13. Methods of effecting interesterification as claimed in Claim 1 and substantially as hereinbefore described with reference to the 10 examples.

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